

Formation of Carbon Nanotube/Glucose-Carrying Polymer Hybrids by Surface-Initiated, Atom Transfer Radical Polymerization

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Introduction

Due to the unique mechanical, electrical, thermal, and optical properties, carbon nanotubes (CNTs) have been investigated for nanoelectronics, electron field emitters, and other applications.¹ CNTs have unique atomic structures, high aspect ratio, and extraordinary mechanical properties such as strength and flexibility, which also make CNTs ideal reinforcing materials in polymer nanocomposites.² In the fabrication of CNT-based polymer composites, the difficulty mainly lies in the fact that CNTs tend to form bundles and it is not easy to separate the bundles of CNTs due to low surface energy of the outer walls of CNTs.³ In CNT/polymer composites prepared by simple mixing, generally polymers can not penetrate the bundles of CNTs and therefore CNTs are not dispersed individually into a polymer matrix. As an alternative to the simple mixing/blending, the chemical attachment of polymers to CNTs has also been attempted to functionalize CNTs for the formation of composites. Sun and his co-workers have investigated “grafting-onto” approach to the fabrication of CNTs with polymers.⁴ For example, Carroll and Sun reported grafting of poly(propionylethylenimine-co-ethylenimine) to single-walled carbon nanotubes (SWCNTs) via amidation.^{4c} Recently, another app-

roach, “grafting-from” approach (in other words, surface-initiated polymerization (SIP)) has intensively been utilized for grafting polymers onto CNTs, because of its advantages over the “grafting-onto” approach⁵ in comparison with the “grafting-onto” technique, SIP usually yields a strong bond between polymers and substrates, a high polymer grafting density, and a possibility of growing block copolymers by a sequential addition of monomers.⁶ As an example of SIP from CNTs, Dai and Waymouth reported surface-initiated, ring-opening metathesis polymerization of norbornene from SWCNTs, where the attachment of a polymerization initiator was achieved by physisorption of pyrenyl group to the wall of SWCNTs.^{5d} Although they were successful in polymerizing norbornene from SWCNTs, they observed the detachment of the growing polymer from SWCNTs over the reaction time, probably because of a decreasing ability of the pyrenyl group to effectively anchor the polymers due to the relatively weak noncovalent interaction between the pyrenyl group and SWCNTs. We also have previously reported the formation of shortened SWCNT (s-SWCNT)/poly(*p*-dioxanone) (PPDX) hybrid composites by surface-initiated, ring-opening polymerization (SI-ROP) of PDX from hydroxyl group-presenting s-SWCNTs, where a polymerization initiator was covalently bound to s-SWCNTs via amide bond.^{5e}

In addition to the fabrication of simple CNT/polymer composites for optimizing the physicochemical, mechanical, and electrical properties of the composites exemplified above, where the properties of interest mainly come from CNTs, the fabrication of functionalized CNTs coupled with a well-defined *biologically (or chemically) functional layer* would yield another level of applications of the composites, such as biocatalysis and biosensors, where the properties of interest synergistically come from both CNTs and functional polymers. For example, Dordick and Ajayan reported the enhanced biocatalytic activity of α -chymotrypsin (CT) in SWCNT/polymer/CT composites, which were formed by simple mixing.⁷ Recently, Sun and co-workers mimicked the multivalent interactions between polysaccharide ligands and lectin (sugar-binding protein) receptors based on the surface functionalization of CNTs:⁸ 2'-aminoethyl- β -D-galactopyranoside was coupled to SWCNTs via amidation, and the bio-specific interaction between galactose-presenting SWCNTs and *Escherichia coli* was demonstrated by cell agglutination assay. Keeping in mind that most of biologically important interactions are multi- or polyvalent and one of the important biological recognitions/interactions is the one between polysaccharides and lectins (or other receptors), we initiated a research program where various mono- and polysaccharides are controllably coupled to CNTs (yielding CNT/glycopolymer hybrids) for the possible applications to biosensing. In this paper we report the first example of

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CNT/glycopolymers hybrid composites, where the polymer was grafted onto shortened multi-walled carbon nanotube (s-MWCNT) by the "grafting-from" technique and the polymer backbone contained biologically active glucose. We used s-MWCNTs to form the composites, because as a proof-of-principle it would be practically easier to deal with MWCNTs than SWCNTs in terms of processibility and characterizability, and the same chemical processes can be applied to SWCNTs when needed for certain applications.

Experimental

Materials. MWCNTs employed in this study were purchased from Iljin Nanotech Co., Ltd (degree of purity: >95%, length: 2~20 μm , diameter: 0.8~1.2 nm). 3-*O*-Methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpGlc)⁹ and 2-lactobionamidoethyl methacrylate (LAMA)¹⁰ were synthesized by following the reported procedures. CuBr(I), 2,2'-dipyridyl, triethylamine, 4-dimethylaminopyridine (DMAP), 6-amino-1-hexanol and 2-bromopropionyl bromide were purchased from Aldrich and used as received. Chloroform (from Aldrich), thionyl chloride (from Fluka), toluene, tetrahydrofuran (THF), sulfuric acid, hydrochloric acid, hydrogen peroxide (from Junsei), formic acid and acetone (from Aldrich) were used without further purification. Ultrapure water (18.3 $\text{M}\Omega \cdot \text{cm}$) from the Human Ultra Pure System (Human Corp., Korea) was used. All other solvents and reagents were of analytical-grade quality and used as received, unless otherwise described.

Instrumentation. Infrared (IR) spectra were recorded using an FTIR spectrophotometer (Bruker, EQUINOX 55). Background spectrum was acquired by averaging 128 scans with 2 cm^{-1} resolution. Scanning electron microscopy (SEM) images were obtained with a scanning electron microscope (Philips, XL30SFEG). Atomic force microscopy (AFM) experiments were carried out on a Digital Instrument (DI) NanoMan atomic force microscope with a Nanoscope IV controller. Tapping mode of the operation with Nanoscope IIIa software version 5.12b48 was used to produce high-resolution surface images. The thermal characteristics of the s-MWCNT/polymer hybrids were measured by thermogravimetric analysis (TA Instruments, TGA 2050). Centrifugation was carried out using a MF-600 ultracentrifuge (Hanil Science Industrial).

Oxidation and Cutting of Carbon Nanotubes. The chemical oxidation of purified MWCNTs was carried out by refluxing nanotubes in a 2.6 M aqueous solution of nitric acid (HNO_3) for 48 h at 120 $^\circ\text{C}$.¹¹ After reflux, the resultant was then washed with distilled water 3 times using centrifuge. The oxidized MWCNTs were gathered, washed with acetone, and dried under vacuum overnight. Cutting of MWCNTs was carried out in an acid mixture of sulfuric acid and nitric acid (3:1), known as aqua regia: MWCNTs (1 g) were sonicated in a mixture (500 mL) of concentrated

H_2SO_4 and HNO_3 (3:1) for 24 h at temperatures between 35 and 40 $^\circ\text{C}$ (Bransonic, model 1510). The resultant was diluted with 2 L of distilled water, and then centrifuged in distilled water 3 times. The resulting MWCNTs were polished in a mixture of concentrated H_2SO_4 and 30% aqueous H_2O_2 (4:1) under sonication for 24 h at temperatures between 35 and 40 $^\circ\text{C}$. The prepared s-MWCNTs were washed with distilled water several times, and then added to 1 M HCl solution to regenerate the terminal carboxylic acid on s-MWCNTs. Finally the s-MWCNTs were centrifuged to remove remaining acid solution, and dried under vacuum overnight.

Introduction of ATRP Initiators onto s-MWCNTs. To functionalize s-MWCNTs with acid chloride, 50 mg of the carboxylic acid-functionalized s-MWCNTs were dried under vacuum and then suspended in 50 mL of thionyl chloride (SOCl_2) in an ultrasonic bath. The dispersion was heated under reflux for 24 h to convert the carboxylic acid group into acid chloride. Excess SOCl_2 was immediately removed by rotary evaporator and then the resultant was added to methylene chloride (30 mL) containing 6-amino-1-hexanol (300 mg). The reaction mixture was stirred overnight to form amide bond between 6-amino-1-hexanol and the acid chloride group on s-MWCNTs. After stirring, the resulting s-MWCNT (s-MWCNT-OH) was washed 3 times with CH_2Cl_2 using centrifuge, and then dried under vacuum overnight.

Using the free hydroxyl group of 6-amino-1-hexanol-attached s-MWCNTs, 2-bromo-2-methylpropionyl bromide was coupled to s-MWCNTs via ester linkage. s-MWCNT-OH (50 mg) was placed in 30 mL of anhydrous CHCl_3 , and then 30 mg of DMAP and 0.3 g of triethylamine were added to the solution. 2-Bromo-2-methylpropionyl bromide (0.4 g) dissolved in 5 mL of CHCl_3 was added to the reaction mixture dropwise at 0 $^\circ\text{C}$ for 1 h. The resulting mixture was stirred for 3 h at 0 $^\circ\text{C}$ followed by stirring 48 h at room temperature. After stirring, the resultant was washed 3 times with CH_2Cl_2 using centrifuge and then dried under vacuum overnight. The purification yielded the initiator-presenting s-MWCNT (s-MWCNT-Br).

Formation of s-MWCNT/Glucose-Carrying Polymer Hybrids. s-MWCNT-Br (30 mg), CuBr (5 mg), 2,2'-dipyridyl (11 mg), ethanol (nitrogen-purged by freeze-thaw cycle, 20 mL) and water (nitrogen-purged, 5 mL) were placed in a 50-mL two-necked, round-bottomed flask and then the flask was sealed with a glass cock using vacuum grease. The flask was purged with nitrogen and then 1 mL of MAIpGlc monomer was injected by syringe. The mixture was sonicated for 5 min and then stirred for 24 h at room temperature. After stirring, the mixture was washed with ethanol 3 times to remove any remaining monomer. To deprotect MAIpGlc, the s-MWCNT/pMAIpGlc hybrids were mixed with a mixture of formic acid and water (4:1), sonicated for 2 h to disperse the aggregated hybrids, stirred for 72 h at room temperature, and washed with water and acetone to

remove remaining acid.

s-MWCNT-Br (30 mg), CuBr (5 mg), 2,2'-dipyridyl (11 mg) and nitrogen-purged distilled water (20 mL) were placed in 50 mL two-necked, round-bottomed flask and then the flask was sealed with a glass cock using vacuum grease. The flask was purged with nitrogen and then 400 mg of LAMA monomer was injected by syringe. This mixture was stirred for 24 h at room temperature, and the resulting mixture was washed with water and ethanol 3 times to remove remaining monomer.

Results and Discussion

The procedure for forming s-MWCNT/glucose-carrying polymer hybrid nanocomposites consists of simple three steps: (1) introduction of hydroxyl groups on s-MWCNTs, (2) attachment of a polymerization initiator, 2-bromo-2-methylpropionyl bromide, onto the s-MWCNTs, and (3) surface-initiated, atom transfer radical polymerization (SI-ATRP) of glucose-carrying methacrylates from the s-MWCNTs (Figure 1). Atom transfer radical polymerization (ATRP) was adapted for polymerizing glucose-carrying monomers from the surface of s-MWCNTs because ATRP has several advantages over other polymerization techniques, including the precise control over the molecular weight of polymers (the thickness of functional polymer layers in this study) and mild polymerization conditions.¹²

Glycopolymers have attracted a great deal of attention due

to the biologically important functions of saccharides.¹³ The recognition process of saccharides is thought to be cooperative and therefore strongly dependent upon the spatial distribution and the molecular identity of saccharide residues.¹⁴ It is prerequisite for the elucidation of the recognition process and the application to the area of biosensing to develop a method for controlling the structural parameters of glycopolymers. In this study, we used two different glucose-carrying methacrylates: 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucopyranose (MAIpGlc) and 2-lactobionamidoethyl methacrylate (LAMA). MAIpGlc was chosen as a model compound because it has successfully been used in the SI-ATRP from a glass substrate: Fukuka and co-workers reported the controlled growth of pMAIpGlc from the glass substrate and the facile deprotection of MAIpGlc to MAGlc.¹⁵ The use of LAMA (and its derivatives) would be another approach to the formation of various CNT/glycopolymers hybrid composites. LAMA is readily prepared by the coupling reaction between 2-aminoethyl methacrylate and lactobionolactone^{10,16} and in principle we could synthesize any (meth)acrylates carrying a variety of saccharides (and a sequence of saccharides). In addition, the ATRP of LAMA-based homo- and block copolymers is reported to proceed in a controlled manner.

MWCNTs were oxidized by refluxing them in 2.6 M of HNO₃ for 48 h at 120 °C, and then cut by sonicating the oxidized MWCNTs in aqua regia (H₂SO₄:HNO₃=3:1) for 24 h at temperatures between 35 and 40 °C and in a mixture

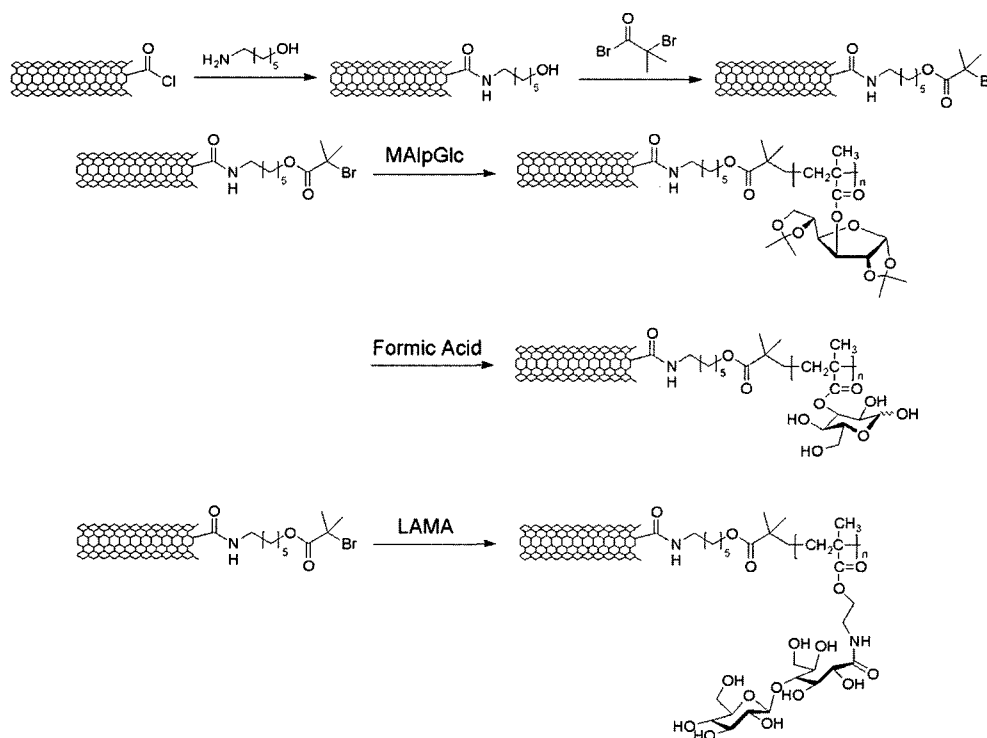


Figure 1. Schematic description of the procedure of the formation of s-MWCNT/glucose-carrying polymer hybrids.

of concentrated H_2SO_4 and 30% aqueous H_2O_2 (4:1) for 24 h at temperatures between 35 and 40 °C. After cutting, three characteristic IR peaks were observed at 1720 cm^{-1} (C=O carboxyl group), 1570 cm^{-1} (C=C double bond), and 1100-1200 cm^{-1} (C-O stretching) in the IR spectrum of s-MWCNTs (Figure 2(a) and Table I).¹⁷ In the scanning electron microscopy (SEM) image, the length of s-MWCNTs ranged from 100 to 1000 nm, indicating that one crude MWCNT was broken into about 10 to 100 pieces because the length of crude MWCNTs ranged from 2-20 μm . After the oxidation and cutting, the hydrophilicity of s-MWCNTs was drastically changed. Crude MWCNTs showed no solubility in almost all the organic solvents, and easily aggregated in water and acetone. After the chemical treatment, s-MWCNTs could be dispersed easily in water and acetone.

To assure that the carboxylic group on s-MWCNTs can be used to form amide bond, we attached 1-hexadecylamine onto s-MWCNTs through amide bond as a model. The IR spectrum showed that the peak from C=O stretching of car-

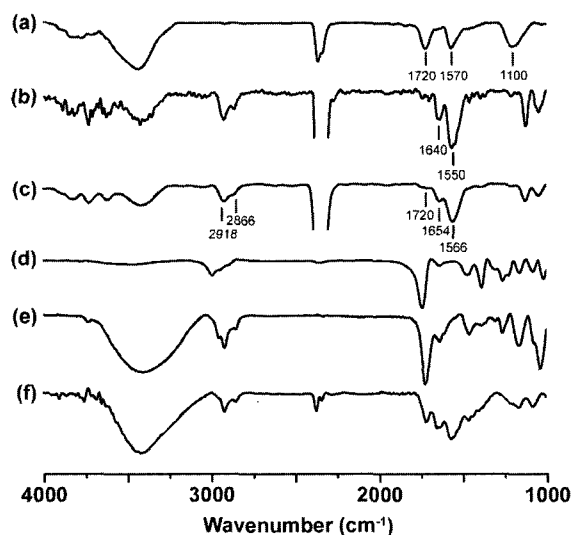


Figure 2. IR spectra of (a) s-MWCNT, (b) 1-hexadecylamine-attached s-MWCNT, (c) initiator-attached s-MWCNT, (d) s-MWCNT/pMAIpGlc hybrid, (e) s-MWCNT/pMAGlc hybrid, and (f) s-MWCNT/pLAMA hybrid.

boxylic acid (at 1720 cm^{-1}) disappeared after the coupling and characteristic IR peaks of amide bond appeared at 1640 and 1550 cm^{-1} (Figure 2(b)). It was practically difficult to detect any peak shift in the IR spectrum after the conversion from COOH to COCl, because the COCl group readily decomposed back to the COOH group under ambient conditions. The attachment of 6-amino-1-hexanol and 2-bromo-2-methylpropionyl bromide onto s-MWCNTs was also confirmed by IR spectroscopy. After the coupling of 6-amino-1-hexanol and the subsequent attachment of the ATRP initiator (yielding s-MWCNT-Br), peaks from amide bond appeared at 1654 and 1566 cm^{-1} in addition to the C-H stretching peaks from the alkyl chains at 2918 and 2866 cm^{-1} (Figure 2(c)). The C=O stretching peak, presumably from the ester linkage, was observed at 1720 cm^{-1} with a weak intensity.

The SI-ATRP of MAIpGlc was carried out by stirring a mixture of s-MWCNT-Br, MAIpGlc, CuBr, and 2,2'-dipyridyl in the EtOH- H_2O solution (4:1) for 24 h at room temperature. No free initiator was added to the reaction system in this study. After the polymerization, s-MWCNTs/pMAIpGlc hybrid composites were thoroughly washed with EtOH, and then dried under vacuum. The IR spectrum of the composite showed characteristic peaks of the protected glucose ring in the range of 1000-1400 cm^{-1} (Figure 2(d)), and the SEM image showed that s-MWCNTs were coated with the polymer but entangled one another (Figure 3(a)). The atomic force microscopy (AFM) image showed dispersed s-MWCNTs/pMAIpGlc hybrid composites, the shapes of which were mainly composed of dog-bone and circular structures (Figure 3(b)). Thermogravimetric analysis (TGA) showed that the polymer content in the composite was about 10% (w/w). The solubility of the resulting composites decreased due to relatively hydrophobic nature of the polymer and they were not dissolved in water or acetone.

The MAIpGlc group is readily deprotected to MAGlc without any degrafting and chain breaking of the grafted polymer. s-MWCNTs/pMAIpGlc hybrid composites were stirred for 72 h at room temperature in a mixture of HCO_2H and H_2O (4:1), thoroughly washed with water and ethanol, and dried under vacuum. After the deprotection (yielding s-MWCNTs/pMAGlc hybrids), the sharp IR peaks from the

Table I. Assignment of IR Peaks at Each Reaction Step

Mode	Band Frequency (cm^{-1})			
	s-MWCNT	initiator-attached s-MWCNT	s-MWCNT/pMAIpGlc hybrid	s-MWCNT/pMAGlc hybrid
$\nu(\text{C-O})$	1100		1000-1400	1000-1400
$\nu(\text{C=C})$	1570			
Amide I, II		1566, 1654		
$\nu(\text{C=O})$	1720	1720	1740	1722
$\nu(\text{CH}_2)$		2918, 2866	2992, 2947, 2902	2954, 2920, 2852
$\nu(\text{O-H})$				3000-3500

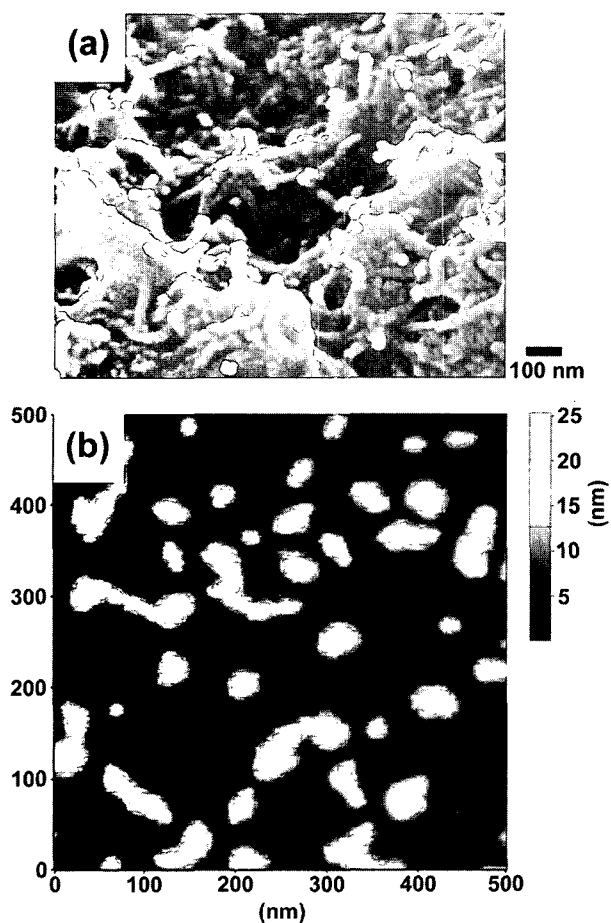


Figure 3. (a) SEM image of s-MWCNT/pMAIpGlc hybrid and (b) AFM image of s-MWCNT/pMAIpGlc hybrid.

protected ring became broad and a broad peak of hydroxyl groups appeared in the range of 3000-3500 cm^{-1} (Figure 2(e)). The solubility of the hybrid was changed: s-MWCNT/pMAIpGlc hybrid composites, carrying hydrophilic glucose moiety, showed improved solubility in water and ethanol.

LAMA was chosen because it does not require any protection/deprotection steps and any arbitrary sugar moiety could be attached to the methacrylate group by the amidation reaction. LAMA is insoluble in methanol and the ATRP of LAMA was relatively uncontrolled in water ($M_w/M_n=1.6-1.8$).¹⁰ Although the best known solvent for the ATRP of LAMA is *N*-methyl-2-pyrrolidone (NMP, $M_w/M_n=1.2$) for the controlled polymerization, we chose water as a solvent system because the M_n of pLAMA is highest in water. The SI-ATRP of LAMA was carried out by stirring an aqueous solution of s-MWCNT-Br, LAMA, CuBr, and 2,2'-dipyridyl for 24 h at room temperature. The IR spectrum confirmed the successful grafting of pLAMA onto s-MWCNTs: characteristic IR peaks of the sugar ring appeared in the range of 1100-1400 cm^{-1} and the IR peak of hydroxyl group in the range of 3000-3500 cm^{-1} (Figure 2(f)).

Conclusions

In conclusion, we demonstrated that SI-ATRP could be utilized for generating CNT/glycopolymer hybrid nanocomposites. As a proof-of-concept, we grafted MAIpGlc, a monomer that carries protected glucose ring, onto s-MWCNTs. After coating s-MWCNTs with pMAIpGlc, the MAIpGlc moiety was deprotected to extrude the glucose group onto the surface of s-MWCNTs. LAMA (and its derivatives) would have advantages over MAIpGlc, because various monosaccharides and a sequence of saccharides could be incorporated into the polymer backbone and polymerization does not need protection/deprotection steps. Considering the biological importance of polysaccharides, the method described herein would be beneficial in many areas, such as pathogen detection and biosensors.

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